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ESTIMATIONS OF THE ISOMER MÖSSBAUER SHIFTS FOR TETRAOXOFERRATES USING ADF PACKAGE

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Abstract. ^{7}Fe isomer shifts and the electron density on iron nucleus for a range of tetraoxoferrate ions have been analyzed by means of DFT calculations. The bond lengths and the electron density on the nuclei obtained by our calculations substantially corresponded to the known structural and Mössbauer data. For ferrates the isomer shift depends on the 4s-orbital population. The results obtained allowed us to estimate the isomer shifts for tetraoxoferrate(VII), $KFeO_4$, and iron(VIII) oxide, FeO_4.

1. Introduction

There is constantly growing interest in iron in high oxidation states primarily due to its high potential in water treatment [1, 2]. Ferrates of alkali metals contain complex tetraoxoferrate anions $[FeO_4]^{n-}$(n=4÷2), which give ferrate(VI)-anion, FeO_4^{2-}, when come into water. FeO_4^{2-}-ion is a very powerful oxidant. They are able to neutralize extremely toxic substances, whereas common oxidizing agents used in water treatment, such as chlorine and ozone, often result in more toxic products. Ferrates (VII) and (VIII) are exotic part of modern inorganic chemistry. But these compounds could be much stronger oxidizers than ferrate (VI). That is why it is very important to know their Mössbauer parameters. This could allow us to detect iron (VII) and (VIII) in the reaction mixture betimes and to optimize the synthetic way.

2. Calculations

To calculate the geometrical parameters of the isolated ions $[Fe^{m}O_4]^{m-8}$ (m>3) obtained with using Amsterdam Density Functional. Geometry optimisation for ions calculated with using exchange functional OPTX [3] conjunction with PBE correlation functional [4] and all-electron TZP basis set of Slater`s o-orbitals, using approximation of frozen core in attitude to core electrons. A scalar relativistic effect was considered with using regular approximation of zero-order ZORA [5]. The applying of this basis set is better with respect to accuracy and efficiency. The analysis of the atomic charge and populations of atomic orbitals has been done using the NBO [6] approximation within the GAUSSIAN'03 [7] program.

Isomer shifts in this paper are related to α-iron and are presented in [mm·s^{-1}].

3. Results and discussion

First, the geometries of ions $[FeO_4]^{n-}$(n=0÷4*)* were optimized by the above mentioned procedure. The calculated Fe-O bond lengths are presented in Table 1. To check the accuracy of our quantum-chemical calculations it is necessary to compare the experimental and calculated geometries of molecules. For the comparison we used the structural data for the following known ferrates: Na_4FeO_4 [8], K_3FeO_4 [9], K_2FeO_4 [10, 11]. In these compounds iron is in practically regular tetrahedral oxygen arrangement. The average Fe-O distances used for comparison are presented in Figure 1.

The correlation diagram is presented in Figure 1 and gives us very good results:

$$R^{exp.}_{Fe-O}[Å] = -0.5 + 1.3R^{cal.}_{Fe-O}[Å] \quad (r=0.999;\ s=0.004;\ n=3)$$

Obtained earlier [15] by B3LYP/DGDZVP method with using Gaussian 03 program suchcorrelation

wasapproximatelythe same quality

$$R^{exp.}_{Fe-O}[Å] = -0.2 + 1.1R^{cal.}_{Fe-O}[Å] \quad (r=0.987;\ s=0.02;\ n=3)$$

In this and subsequent correlation equations r is a correlation coefficient, s is the standard curve fit error, and n is the number of compounds.

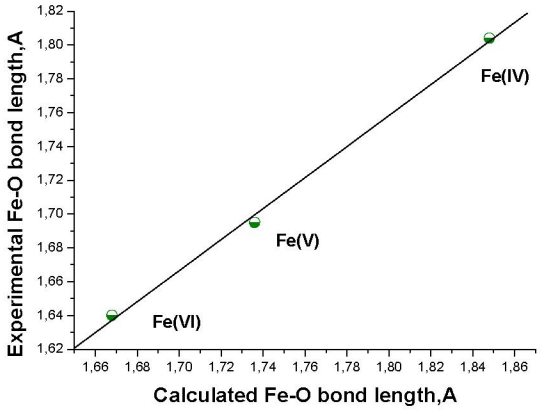

Figure 1. Dependence between experimental and calculated by BP86/TZ2P+ method Fe-O bond length

Basically, for obtaining of dependences between formal degrees of oxidation of the iron ions it is possible to use various schemes of the calculation of different effective charge on atoms. In this paper we used the analysis of an effective charge by Voronoi scheme [16] which is considered one of optimal for estimation atomic charges.

The calculations showed that the increasing of the iron oxidation state (OS) lead to decreasing both natural charge on the oxygen atom (Q_O)and natural charge of the iron atom (Q_{Fe}). The respective dependencies are described by the following correlation equations:

$$Q_O\ [e] = -2.0 + 0.24OS \qquad (r = 0.9999;\ s = 0.007;\ n = 7)$$
$$Q_{Fe}\ [e] = 0.1 + 0.03OS \qquad (r = 0.982;\ s = 0.01;\ n = 7)$$

Increasing of the oxidation state is also accompanied by the increase of the electron density on the iron nucleus(ρ_0) (Figure 2.)

$$\rho_0\,[a_0^{-3}] = 14824 + 1.06OS \quad (r = 0.982;\ s = 0.5;\ n = 7)$$

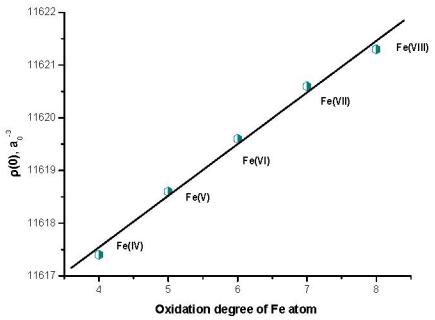

Figure 2. Dependence between electron density on Fe nuclei (calculated by BP86/TZ2P+ method) and ions oxidations state

Table 1. Optimized by BP86/TZ2P+ method and experimental parameters for tetraoxoferrates (IV) – (VIII)

Oxidation state of iron	$R^{cal.}_{Fe-O}$, Å	$R^{exp.}_{Fe-O}$, Å	$\delta^{cal.}_{\alpha-Fe}$, mm·s^{-1}	$\delta^{exp.}_{\alpha-Fe}$, mm·s^{-1}	ρ_0, a_0^{-3}	N_s, e
+4	1.848	1.804 for Na_4FeO_4	-0.18	-0.22 for Na_4FeO_4	14827.0	0.223
+5	1.736	1.695 for K_3FeO_4	-0.55	-0.55 for K_3FeO_4	14828.7	0.241
+6	1.668	1.640 for K_2FeO_4	-0.87	-0.90 for K_2FeO_4	14830.1	0.255
+7	1.619	-	-1.18	-	14831.3	0.268
+8	1.586	-	-1.40	-	14832.3	0.277

The similar correlation presented earlier [15] had a few more correlation parameter, but ions Fe(II) and Fe (III) are excluded from correlation dependence calculated by B3LYP/dgdzvp

$$\rho_0 [a_0^{-3}] = 11613.6 + 0.98\,OS \qquad (r = 0.996;\ s = 0.16;\ n = 5)$$

Finally ρ_0 has been compared with experimental isomer shifts of well-known ferrates (Figure 3). This dependency has also good correlation parameters:

$$\delta [mm \cdot s^{-1}] = 2997 - 0.20215\rho_0 [a_0^{-3}] \qquad (r = 0.980;\ s = 0.07;\ n = 3)$$

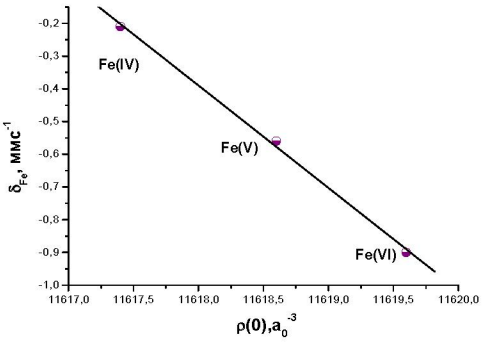

Figure 3. Dependence between experimental shift and calculated relativistic electronic densities at the ^{57}Fe nucleus (by BP86/TZ2P+ method)

The correlation dependences obtained by both methods have allowed to use calculated electronic density on Fe nucleus to estimate of isomer shifts for tetraoxoferrate (VII) and (VIII) (-1.18 and -1.40 mm·s^{-1} from B3LYP/dgdzvp method [15], as well as -1.15 and -1.35 mm·s^{-1}from BP86/TZ2P+ method, in this paper, relative to α-Fe respectively). Obviously, using of different methods of calculation has allowed obtaining almost identical isomer shifts which indicates asufficientlyprecisionof these calculationsandtheir proximityto the experimental values.

It will be noted that absorption lines in the respective range were already observed formerly at the spectra of Na_4FeO_4 [12]. This compound decomposes at room temperature by disproportionation mechanism. During this multistage process several higher oxidation states of iron can be observed. Interaction of Na_4FeO_4 with Na_2O_2 also allowed us to synthesized iron derivatives showing absorption lines with extremely low shifts [12]. The line with isomer shift -1.52 mm·s^{-1} (at 78 K) was also observed in the frozen solutions, obtained by anodic dissolution of metallic iron in concentrated NaOH (14M NaOH) at high current densities [17]. This line was assigned to Fe(VIII).

It is well known that for Mössbauer atoms the magnitude of the isomer shift depends simultaneously on the s-, p- and d-orbital populations of these atoms [18]. Earlier for various so-called Mössbauer atoms

very good correlations between isomer shifts and orbital populations calculated at B3LYP/3-21G(d) by similar procedure have been found [19-22]. For iodine compounds the main contribution to isomer shift comes from the 5s-orbital population, but for tin and antimony compounds a considerable contribution comes from the shielding by 5p-orbitals. For the Au(I) and Au(III) compounds the dependences between the isomer shift and the orbital populations include the direct effect of the valence-shell s-electrons and their shielding of the d-electrons. According to these results it was possible to confirm the conclusion about the greater contribution of the 6s-orbital than 5d-orbital of a gold atom to the isomer shift. If in Au(I) compounds the chemical bonding is determined basically by s- and to a lower extent by d-orbitals of the central atom, in Au(III) compounds the contribution of d-orbital is considerably increased, that is coordinated by a natural image with the increase of the number gold atom bonds. The similar results were obtained by us at B3LYP/LanL2DZ level of Pt(II) and Pt(IV) compounds [20]. For Pt(II) compounds the main contribution to isomer shift comes from the 6s-orbital population, but for Pt(IV) compounds the shielding of the nucleus by 5d-orbitals brings in the greater contribution.

The main observed trends in the variations of the isomer shifts for ferrates can now be interpreted in terms of the valence electronic populations, which depend on iron oxidation state. Our calculation leads to the conclusion that in tetraoxoferrate ions the main contribution to isomer shift brings the 4s-electrons, which is confirmed by the excellent correlation equation:

$$\delta[mm \cdot s^{-1}] = -0.214 - 0.045N_S\,[e] \qquad (r=0.999;\ s=0.001;\ n=5)$$

This correlation is valid for both calculated and experimental isomer shifts of ferrates (IV)-(VIII).

An addition of the N_d population increment to the last equation impairs the quality of the correlation; the standard curve fit error being 0.01 $mm \cdot s^{-1}$. Thus, our calculations show that the shielding of the iron nucleus by d-electrons does not influence on the isomer shift.

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Оценка изомерныхмессбауэровскихсдвигов для тетраоксоферратов с помощью ADF пакета

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Ключевые слова: теория функционала плотности, ADF(Амстердамский функционал плотности), мессбауэровская спектроскопия, ферраты

Аннотация.С помощью расчетов DFT (теория функционала плотности) были проанализированы изомерные сдвиги ^{57}Feи электронная плотность на ядрахжелеза для ионов тетраоксоферратов. Полученные по нашим расчетамдлины связей и плотность электронов на ядрах хорошо согласуются с известными структурными и мессбауэровскими данными. Для ферратов изомерныесдвигизависят от заселенности 4s-орбитали. Полученные результаты позволили оценить изомерные сдвиги для тетраоксоферратов (VII), $KFeO_4$ и оксида железа (VIII), FeO_4.

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Түйін сөздер: тығыздық функционалының теориясы, ADF (тығыздықтың Амстердам функционалы), мессбауэр спектроскопиясы, ферраттар.

Аннотация. DFT(тығыздық функционалы теориясы) есептеулер көмегімен ^{57}Fe изомерлік ығысулары және тетраоксоферраттар иондары үшін темір ядросындағы электрондық тығыздықтары талданды. Біздің есептеулер бойынша алынған байланыс ұзындығы мен ядролардағы электрондардың тығыздықтары белгілі құрылымдық және мессбауэр мәліметтермен жақсы сәйкес келеді. Ферраттар үшін изомерлік ығысулар 4s-орбиталінің тығыздығына тәуелді болады. Алынған нәтижелер тетраоксоферраттар (VII), $KFeO_4$және темір оксідінің (VIII), FeO_4 изомерлік ығысуларын есептеуге мүмкіндік берді.

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